

OXIDATION OF SATURATED HYDROCARBONS BY AIR IN ACETONITRILE IN THE PRESENCE OF MOLYBDENUM OR TUNGSTEN CARBONYLS DURING LIGHT IRRADIATION*†

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Light irradiation ($\lambda > 310$ nm) in air of alkane solutions in CH_3CN in the presence of catalytic amounts of $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ leads to the formation of oxygenation products (alkyl hydroperoxide, alcohol and ketone). The reaction proceeds with an induction period, during which, under the action of light and molecular oxygen, polynuclear oxo complexes of Mo or W are evidently formed, and these catalyse the photochemical hydroperoxidation of alkane.

In 1989, several groups of researchers produced simultaneous reports on the possibility of the effective oxidation of saturated and alkylaromatic hydrocarbons by molecular oxygen during photocatalysis with oxo complexes of W and Mo [2–7]. Similar oxidation catalysed by oxo compounds of chromium(VI) [8, 9] and chromium(IV) [1] is less convenient, since in this case irreversible reduction of the catalytic complex to the Cr(III) derivative seems to occur during the process. It was of interest to investigate the possibility of using other compounds of group VI metals as photocatalysts for hydrocarbon oxidation. In the present work, carbonyls of these metals were used as such catalysts. Some of the work was published earlier in the form of a brief report [10].

EXPERIMENTAL

Experiments on oxidation were carried out in air in glass cylindrical vessels (2 cm diameter) equipped with jackets cooled with running water ($\sim 15^\circ\text{C}$). The solution, the total volume of which was 5 or 10 ml, was stirred vigorously using a magnetic stirrer. The full light of a DRSh-100 high-pressure mercury lamp (1000 W) was used for irradiation. Specimens of the reaction solution were analysed by means of GLC (LKhM-80/6 chromatograph, column length 2 m, diameter 4 mm, sorbent INERTON AW-HMDS 315–320 μm impregnated with 5% Carbowax 1500, carrier gas argon). In some cases, in order to determine alkylhydroperoxide, the solution was also analysed after its reduction by triphenylphosphine (see [11]).

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RESULTS AND DISCUSSION

During irradiation with the full light of a high-pressure mercury lamp in a glass vessel ($\lambda > 310$ nm) in air in a CH_3CN solution in the presence of $\text{Mo}(\text{CO})_6$, cyclohexane is oxidized by molecular oxygen, forming cyclohexylhydroperoxide, cyclohexanol and cyclohexanone. (The total concentration was defined as the total concentration of alcohol and ketone during elution of a solution not reduced by triphenylphosphine.) The kinetics of accumulation of the oxygenation products is shown in Fig. 1 (curve *a*). As can be seen, the reaction proceeds with an induction period, and the total product yield amounts to 12 molecules per molybdenum carbonyl molecule. In the first few hours of irradiation, in the spectrum of the reaction solution a new band emerges with $\lambda_{\text{max}} = 748$ nm (Fig. 2*a*). Three hours after the start of irradiation the maximum intensity of this band is observed, after which absorption in the longwave region begins to decrease. Note that the peak of the band roughly coincides with the maximum accumulation rate of the oxygenation products of cyclohexane (Fig. 1, curves *a* and *b*).

Tungsten carbonyl also catalyses the photo-oxidation of cyclohexane. In this case we determined the concentration not only of the stable products (cyclohexanol and cyclohexanone), but also of the intermediate cyclohexylhydroperoxide (for this, the reaction solution at the initial moment in time was analysed twice — before and after reduction of the specimen of the solution by excess triphenylphosphine, as described in [11]). The accumulation of cyclohexylhydroperoxide and total alcohol and ketone in time is shown in Fig. 3 (curves *a* and *b*). Both final and intermediate products are evidently formed after the induction period. Furthermore, the kinetic curves indicate that the alcohol and ketone are formed during decomposition of the hydroperoxide. As a result of the reaction, after 12 hr irradiation, about 9 molecules of products per photocatalyst molecule are produced. The process is accompanied by changes in the absorption spectrum of the reaction solution, shown in Fig. 2*b*. As in the case of reaction with $\text{Mo}(\text{CO})_6$, here there is an initial increase and then a drop in intensity of the band in the longwave region (Fig. 3, curve *c*). However, in a reaction catalysed by $\text{W}(\text{CO})_6$, the maximum

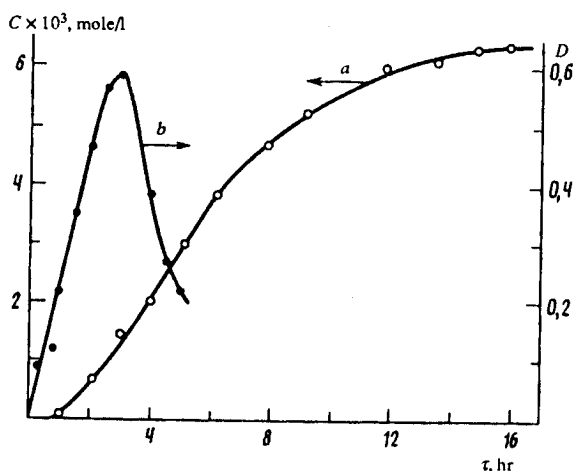


FIG. 1. Change, with time, in the concentration of oxidation products (total) (*a*) and in the intensity of absorption of the reaction solution at $\lambda = 748$ nm (*b*) during the photo-oxidation of cyclohexane (0.46 mole/l) in the presence of $\text{Mo}(\text{CO})_6$ (5×10^{-4} mole/l) in CH_3CN .

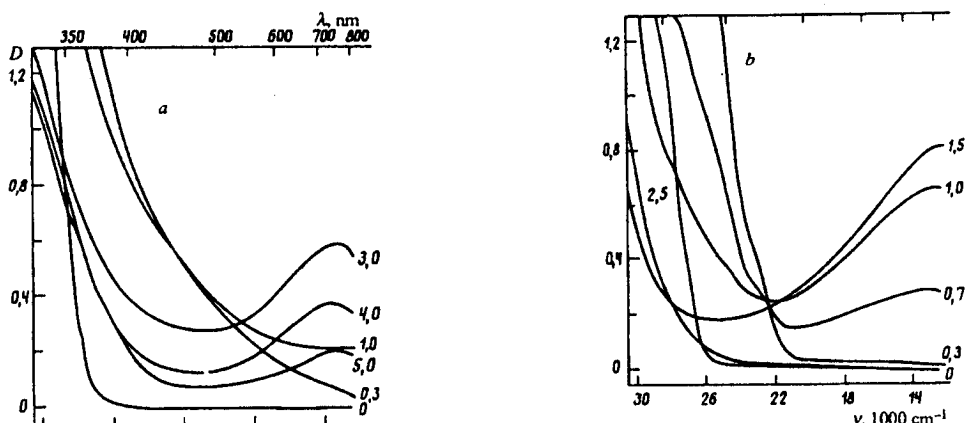


FIG. 2. Change in the absorption spectra of reaction solutions during the photo-oxidation of cyclohexane in the presence of $\text{Mo}(\text{CO})_6$ (a) (conditions as in Fig. 1) and $\text{W}(\text{CO})_6$ (b) (conditions as in Fig. 3). The figures by the curves indicate the time (hr) from the start of irradiation of the solution. A Specord UV-VIS spectrophotometer was used.

intensity of the band at $\lambda \sim 800$ nm falls at a time (1.5 hr) where the rate of accumulation of oxidation products of cyclohexane is still insignificant.

Tungsten and molybdenum carbonyls also catalyse similar reactions of photo-oxygenation of other saturated and also alkylaromatic hydrocarbons. Thus, after irradiation for 5 hr of a solution of *n*-heptane (0.76 mole/l) and $\text{W}(\text{CO})_6$ (5×10^{-4} mole/l) in CH_3CN , after the addition of triphenylphosphine it was possible to determine the regioselectivity in the formation of alcohols and hydroperoxides: C(1)/C(2)/C(3)/C(4) = 1:6:3:5:4:5. During the oxidation of 3-methylhexane, an assessment was made of the ratio of the reactivities at the tertiary and second-

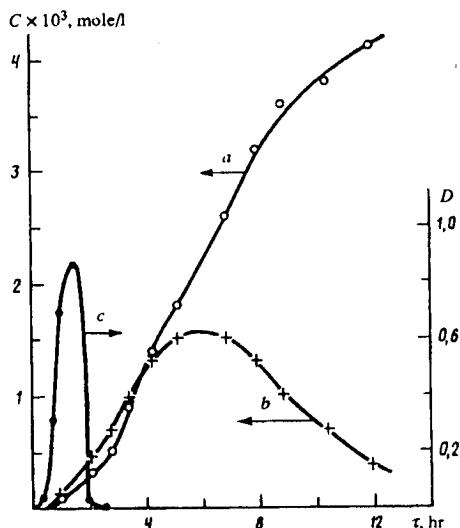


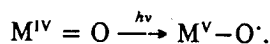
FIG. 3. Change in the concentration of cyclohexanol and cyclohexanone (total) (a) and cyclohexylhydroperoxide (b) and in the intensity of absorption of the reaction solution at $\lambda = 800$ nm (c) during the photo-oxidation of cyclohexane (0.46 mole/l) in the presence of $\text{W}(\text{CO})_6$ (5×10^{-4} mole/l) in CH_3CN .

dary carbon atoms ($\cong 1:15$). The oxidation of ethylbenzene (0.46 mole/l) in the presence of $W(CO)_6$ (5×10^{-4} mole/l) for 10 hr yielded, after reduction by triphenylphosphine, 2.2×10^{-3} mole/l of acetophenone and 1.9×10^{-3} mole/l of 2-phenylethanol. The competing oxidation of cyclohexane (0.46 mole/l) and ethylbenzene (2.76 mole/l) showed that the C-H bond of the methylene group of ethylbenzene is 11 times more active than that in cyclohexane. This parameter (see [12]) was equal to 8.5 in the case of $Mo(CO)_6$ photocatalysis.

It must be noted that, in attempts to carry out the oxygenation of cyclohexane, photocatalysed by carbonyl $Cr(CO)_6$, we succeeded in recording the formation of products of hydrocarbon oxidation in appreciable concentrations.

Discussing the mechanism of alkane photooxygenation catalysed by Mo and W carbonyls, it can be assumed that, at the initial moment of the reaction, oxidation of the carbonyl occurs with the formation of particles containing M=O fragments, where M is Mo or W. The formation of these particles possibly occurs after detachment of one or several CO ligands from $M(CO)_6$ under the action of light and the reaction of the coordination-unsaturated complex with an oxygen molecule. Several particles with M = O fragments (and, possibly, also carrying CO ligands) combine to form polyoxometallate clusters. Since in these clusters the metal atoms are not only in a higher state of oxidation (+6), but also in a lower state of oxidation (+5), absorption bands appear in the longwave (700–800 nm) region in the spectra of solutions [13]. Comparing Figs 1 and 3 it can be assumed that, in the case of $Mo(CO)_6$, a partially reduced particle is the photocatalyst, while reaction with $W(CO)_6$ is catalysed chiefly by a completely oxidized particle.

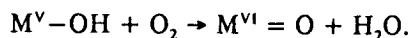
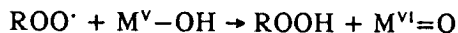
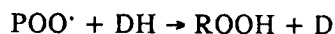
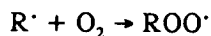
Thus it is evident that photoinduced oxidation of carbonyls by molecular oxygen occurs during the induction period of the reaction, resulting in the formation of catalytically active multinuclear particles containing $M^{VI}=O$ bonds. Photoexcitation of such a particle leads to charge transfer, which can be depicted nominally by the equation



An excited radical-like particle detaches a hydrogen atom from the alkane



Then the process can proceed in the following way:



Here DH is the molecule that is the hydrogen atom donor; the M-OH complex can also be a hydrogen atom donor. This results in the accumulation of alkylhydroperoxide, which partially decomposes (under the action both of the metal complex and of light) with the formation of alcohol and ketone.

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